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• **PACHLA R R ET AL: "STUDIES ON VINYL ESTER
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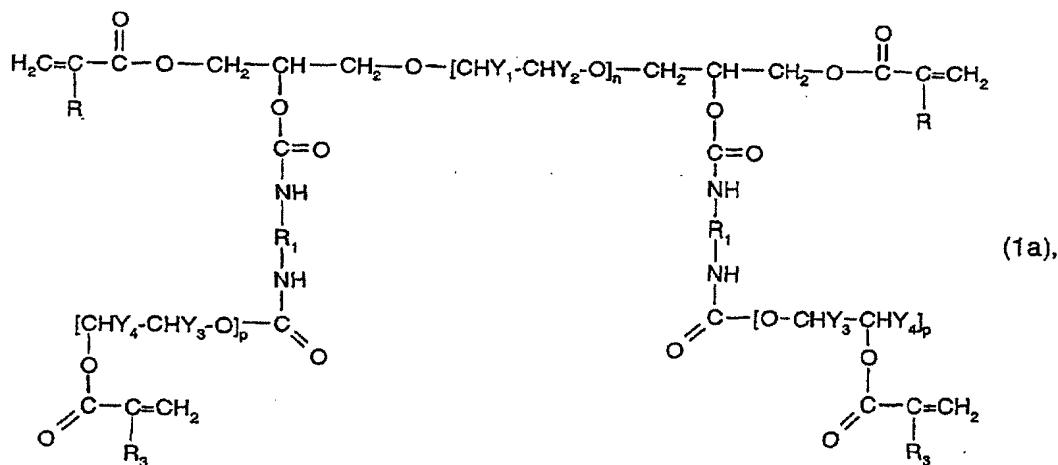
Description

[0001] The present invention relates to novel polyoxyalkylene-unit-containing block copolymers having a number of crosslinkable side groups, to a process for the preparation thereof, and to the use thereof in the production of mouldings, especially ophthalmic mouldings, such as contact lenses.

[0002] A tetraacrylate that is obtained by reacting a polypropylene glycol diglycidyl acrylate with a diisocyanate and a hydroxyethyl acrylate, and the use thereof as a formulation component in resin mixtures for stereolithographic processes, is already known from EP-A-0 614 122.

[0003] It has now surprisingly been found that specific crosslinkable polyether copolymers are especially suitable for the production of ophthalmic mouldings, such as, for example, contact lenses.

[0004] The present invention relates to a contact lens obtainable by crosslinking a prepolymer that corresponds essentially to formula



wherein

R and R₃ are each independently of the other hydrogen or methyl,
one of the radicals Y₁ and Y₂ is hydrogen and the other is hydrogen or methyl,
R₁ is the radical of a linear or branched aliphatic diisocyanate having from 3 to 24 carbon atoms, the radical of a cycloaliphatic or aliphatic-cycloaliphatic diisocyanate having from 3 to 24 carbon atoms, or the radical of an aromatic or araliphatic diisocyanate having from 6 to 24 carbon atoms,
one of the radicals Y₃ and Y₄ is hydrogen and the other is hydrogen or methyl,
p is an integer from 5 to 100 and
n is an integer from 5 to 100,

in the absence or presence of an additional vinyl comonomer.

[0005] In formula (1a) R is, for example, methyl or, preferably, hydrogen. The variable R₃ is, for example, hydrogen or, preferably, methyl.

[0006] A variant of the prepolymers used in accordance with the invention concerns those in which one of Y₁ and Y₂ is hydrogen and the other is methyl. A further preferred variant of the prepolymers used in accordance with the invention concerns those in which Y₁ and Y₂ are each hydrogen. The variable n is, for example, an integer from 5 to 100, especially from 8 to 50 and more especially from 9 to 25.

[0007] R₁ is preferably linear or branched C₃-C₁₈alkylene or unsubstituted or C₁-C₄alkyl- or C₁-C₄-alkoxy-substituted C₆-C₁₀arylene, C₇-C₁₈aralkylene, C₆-C₁₀arylene-C₁-C₂alkylene-C₆-C₁₀arylene, C₃-C₈cycloalkylene, C₃-C₈cycloalkylene-C₁-C₆alkylene, C₃-C₈cycloalkylene-C₁-C₂alkylene-C₃-C₈cycloalkylene or C₁-C₆alkylene-C₃-C₈cycloalkylene-C₁-C₆alkylene.

[0008] R₁ as alkylene is preferably a linear or branched C₃-C₁₈alkylene radical, especially a linear or branched C₄-C₁₂alkylene radical and more especially a linear, or especially a branched, C₆-C₁₀alkylene radical. Preferred alkylene radicals include 1,4-butylene, 2,2-dimethyl-1,4-butylene, 1,5-pentylene, 2,2-dimethyl-1,5-pentylene, 1,6-hex-

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ylene, 2,2,3- or 2,2,4-trimethyl-1,5-pentylene, 2,2-dimethyl-1,6-hexylene, 2,2,3- or 2,2,4- or 2,2,5-trimethyl-1,6-hexylene, 2,2-dimethyl-1,7-heptylene, 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6-trimethyl-1,7-heptylene, 2,2-dimethyl-1,8-octylene, and 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6- or 2,2,7-trimethyl-1,8-octylene.

[0009] When R₁ is arylene it is especially naphthylene or more especially phenylene. When the arylene is substituted, a substituent is preferably located in the ortho position to an isocyanate group. Examples of substituted arylene are 1-methyl-2,4-phenylene, 1,5-dimethyl-2,4-phenylene, 1-methoxy-2,4-phenylene and 1-methyl-2,7-naphthylene.

[0010] R₁ as aralkylene is especially naphthalalkylene or more especially phenylalkylene. The alkylene group in the aralkylene contains preferably from 1 to 12, especially from 1 to 6, or more especially from 1 to 4 carbon atoms. More especially, the alkylene group in the aralkylene is methylene or ethylene. Examples include 1,3- or 1,4-benzylene, naphth-2-yl-7-methylene, 6-methyl-1,3- or 1,4-benzylene, and 6-methoxy-1,3- or 1,4-benzylene.

[0011] When R₁ is cycloalkylene it is especially C₅-C₆cycloalkylene or more especially cyclohexylene, each of which is unsubstituted or substituted by methyl. Examples include 1,3-cyclobutylene, 1,3-cyclopentylene, 1,3- or 1,4-cyclohexylene, 1,3- or 1,4-cycloheptylene, 1,3- or 1,4- or 1,5-cyclooctylene, 4-methyl-1,3-cyclopentylene, 4-methyl-1,3-cyclohexylene, 4,4-dimethyl-1,3-cyclohexylene, 3-methyl- or 3,3-dimethyl-1,4-cyclohexylene, 3,5-dimethyl-1,3-cyclohexylene and 2,4-dimethyl-1,4-cyclohexylene.

[0012] When R₁ is cycloalkylenealkylene it is preferably cyclopentylene-C₁-C₄alkylene or especially cyclohexylene-C₁-C₄alkylene, each of which is unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, especially methyl. The group cycloalkylenealkylene is more especially cyclohexyleneethylenyl or preferably cyclohexylenemethylene, each of which is unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups. Examples include cyclopent-1-yl-3-methylene, 3-methylcyclopent-1-yl-3-methylene, 3,4-dimethylcyclopent-1-yl-3-methylene, 3,4,4-trimethylcyclopent-1-yl-3-methylene, cyclohex-1-yl-3- or -4-methylene, 3- or 4- or 5-methylcyclohex-1-yl-3- or -4-methylene, 3,4- or 3,5-dimethylcyclohex-1-yl-3- or -4-methylene, and 3,4,5- or 3,4,4- or 3,5,5-trimethylcyclohex-1-yl-3- or -4-methylene.

[0013] When R₁ is alklenecycloalkylenealkylene it is preferably C₁-C₄alklenecyclopentylene-C₁-C₄alkylene or especially C₁-C₄alklenecyclohexylene-C₁-C₄alkylene, each of which is unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, especially methyl. The alklenecycloalkylenealkylene group is more especially ethlenecyclohexyleneethylene or preferably methylenecyclohexylenemethylene, each of which is unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups. Examples include cyclopentane-1,3-dimethylene, 3-methylcyclopentane-1,3-dimethylene, 3,4-dimethylcyclopentane-1,3-dimethylene, 3,4,4-trimethylcyclopentane-1,3-dimethylene, cyclohexane-1,3- or -1,4-dimethylene, 3- or 4- or 5-methylcyclohexane-1,3- or -1,4-dimethylene, 3,4- or 3,5-dimethylcyclohexane-1,3- or -1,4-dimethylene, and 3,4,5- or 3,4,4- or 3,5,5-trimethylcyclohexane-1,3- or -1,4-dimethylene.

[0014] R₁ as C₃-C₈cycloalkylene-C₁-C₂alkylene-C₃-C₈cycloalkylene or C₆-C₁₀arylene-C₁-C₂alkylene-C₆-C₁₀arylene is preferably C₅-C₆cycloalkylenemethylene-C₅-C₆cycloalkylene or phenylenemethylenephenylene, each of which may be unsubstituted or substituted in the cycloalkyl or phenyl ring by one or more methyl groups.

[0015] The radical R₁ is of symmetrical or, preferably, asymmetrical structure.

[0016] In a preferred group of R₁ radicals, R₁ is linear or branched C₆-C₁₀alkylene, cyclohexylenemethylene or cyclohexylenemethylenebis(cyclohexylene) unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, or phenylene or phenylenemethylenephenylene unsubstituted or substituted in the phenyl moiety by methyl.

[0017] Examples of suitable radicals R₁ are the radicals of methylene bis(phenylisocyanate), hexamethylene diisocyanate (HMDI), methylene bis(cyclohexylisocyanate), isophorone diisocyanate (IPDI), tolulylene-2,4-diisocyanate (TDI) and of 1,6-diisocyanato-2,2,4-trimethyl-n-hexane (TMDI).

[0018] In an especially preferred group of R₁ radicals, R₁ is linear or branched C₆-C₁₀alkylene, or cyclohexylenemethylene or cyclohexylenemethylenebis(cyclohexylene) unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups. R₁ is more especially asymmetrical, branched C₆-C₁₀alkylene, or cyclohexylenemethylene substituted in the cyclohexyl moiety by from 1 to 3 methyl groups.

[0019] Variable p is, for example, an integer from 5 to 100, especially from 8 to 50, or more especially from 9 to 25.

[0020] A variant of the prepolymers used in accordance with the invention concerns those prepolymers in which one of the radicals Y₃ and Y₄ is hydrogen and the other is methyl.

[0021] A further preferred variant of the prepolymers used in accordance with the invention concerns those prepolymers in which Y₃ and Y₄ are each hydrogen.

[0022] Special preference is given to prepolymers that correspond essentially to formula (1a) above wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is linear or branched C₆-C₁₀alkylene, cyclohexylenemethylene or cyclohexylenemethylenebis(cyclohexylene) unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, or phenylene or phenylenemethylenephenylene unsubstituted or substituted in the phenyl moiety by methyl, Y₁, Y₂, Y₃ and Y₄ are each hydrogen, and n and p are each independently of the other an integer from 8 to 50.

[0023] Special preference is given to prepolymers that correspond essentially to formula (1a) above wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is asymmetrical, branched C₆-C₁₀alkylene, or cyclohexylenemethylene substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, Y₁, Y₂, Y₃ and Y₄ are each hydrogen,

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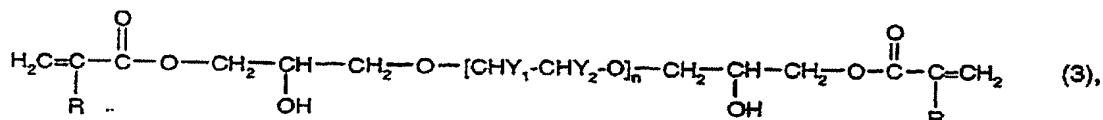
and n and p are each independently of the other an integer from 9 to 25.

[0024] As has already been mentioned, the ophthalmic mouldings according to the invention may be obtained by crosslinking a prepolymer of formula (1a) in the presence or absence of an additional vinyl comonomer. It is furthermore possible also for mixtures of two or more different prepolymers of the above formula (1a) to be used as starting material in the production of the ophthalmic mouldings according to the invention.

[0025] The prepolymers of the above formula (1a), in which the meanings and preferred meanings given above apply to each of the variables therein, are novel and the invention relates also thereto.

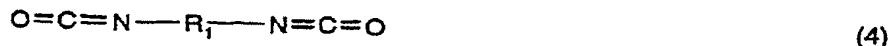
[0026] The prepolymers according to the invention may be prepared, for example, by reacting approximately 1 molar equivalent of a compound of formula

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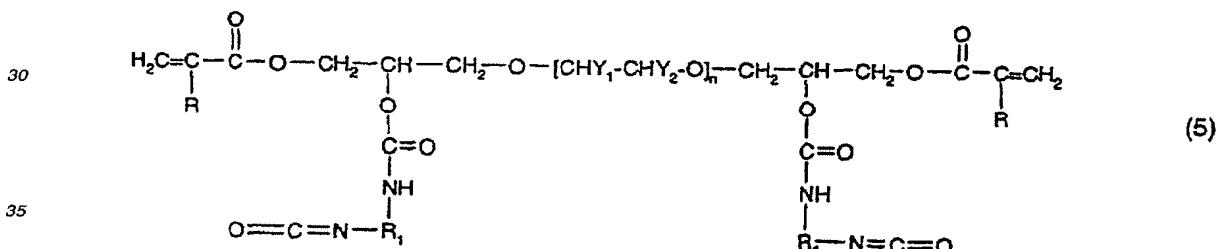


wherein R, Y₁, Y₂ and n are each as defined hereinbefore, with approximately 2 molar equivalents of a diisocyanate of formula

20



25 wherein R₁ is as defined hereinbefore, and then reacting the addition product of formula



obtainable in that reaction with approximately 2 molar equivalents of a compound of formula

40



wherein R₂ is a radical of formula

50



one of the radicals Y₃ and Y₄ is hydrogen and the other is hydrogen or methyl, m is an integer from 4 to 99, and R₃ is as defined in claim 1, to form a prepolymer of formula (1a).

[0027] All of the compounds of formulae (3), (4) and (6) are known or may be obtained in a manner known *per se*. The compounds of formula (3) may be prepared, for example, by reacting a polyalkylene glycol diglycidyl ether with acrylic acid or methacrylic acid in a molar ratio of approximately 1:2. The compounds of formula (6) can be obtained,

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for example, by reacting a reactive acrylic or methacrylic acid derivative, for example the corresponding acid chloride, with equimolar amounts of a polyalkylene glycol of the formula HO-R₂-OH.

[0028] The reaction of the diglycidyl ether of formula (3) with the diisocyanate of formula (4) (1st reaction step) and the further reaction of the addition product of formula (5) with the hydroxy(meth)acrylate of formula (6) (2nd reaction step) are each advantageously carried out in an inert solvent. Suitable inert solvents are aprotic solvents, such as, for example, aliphatic or aromatic hydrocarbons, for example a higher-boiling alkane or alkane mixture, such as petroleum ether, a xylene mixture or toluene; halogenated hydrocarbons, for example chloroform, methylene chloride, trichloroethane, tetrachloroethane, chlorobenzene; ethers, for example tetrahydrofuran, dioxane; ketones, for example acetone, ethyl methyl ketone, dibutyl ketone, methyl isobutyl ketone; carboxylic acid esters and lactones, for example ethyl acetate, butyrolactone, valerolactone; alkylated carboxylic acid amides, for example N,N-dimethylacetamide, N-methylpyrrolidone; nitriles, for example acetonitrile; sulfones and sulfoxides, for example dimethyl sulfoxide, tetramethylenesulfone. Mixtures of several of the mentioned solvents are also possible.

The reaction temperature in both the first reaction step and the second reaction step is, for example, from -5°C to 150 °C, especially from 0 to 100°C, more especially from 20 to 80°C. It is furthermore preferable for both the reaction of the hydroxy group-containing component of formula (3) with the diisocyanate of formula (4) and the reaction of the addition product of formula (5) with the hydroxy compound of formula (6) to be carried out in the presence of a catalyst. Suitable catalysts include, for example, metal salts, such as alkali metal salts or tin salts of organic carboxylic acids or tertiary amines, for example (C₁-C₆alkyl)₃N (triethylamine, tri-n-butylamine), N-methylpyrrolidine, N-methylmorpholine, N,N-dimethylpiperidine, pyridine and 1,4-diazabicyclooctane. Tin salts have proved particularly effective, especially alkytin salts of carboxylic acids, such as, for example, dibutyltin dilaurate and tin dioctoate.

[0029] The catalyst is used in the reaction in a ratio by weight of, for example, from 1:10 to 1:1000, especially from 1:50 to 1:750, or more especially approximately from 1:100 to 1:500, based in each case on the component of formula (3) or (5).

[0030] The reaction times may vary within wide limits, it being possible for the progress of the reaction to be monitored satisfactorily by means of the decrease in the isocyanate content of the reaction mixture. Reaction times that have proved practicable are, for example, in the 1st reaction step of the reaction of the compound of formula (3) with the diisocyanate of formula (4), from 0.5 to 12 hours or preferably from 1 to 5 hours and, in the 2nd reaction step of the reaction of the compound of formula (5) with the compound of formula (6), from 1 to 24 hours or preferably from 4 to 16 hours.

[0031] The reaction is advantageously carried out in a one-pot process, for example by reacting the compound of formula (3) with the diisocyanate of formula (4) until the isocyanate content of the reaction mixture has halved, then adding a compound of formula (6), where appropriate dissolved in one of the above-mentioned solvents, and continuing the reaction until virtually no isocyanate can be detected in the reaction mixture.

[0032] A variant comprises using instead of a diisocyanate of formula (3) two or, if desired, more different diisocyanates and/or instead of a compound of formula (6) two or, if desired, more different compounds of formula (6) in the process, resulting in prepolymers comprising a mixture of several different symmetrical and asymmetrical compounds of formula (1a), that is to say prepolymers in which the two R radicals, the two R₁ radicals and/or the two R₃ radicals in the molecule are identical or different.

[0033] The prepolymers obtained are isolated and purified according to methods known *per se*, for example extraction, crystallisation, recrystallisation, ultrafiltration or chromatographic purification methods. The compounds are obtained in high yields and a high degree of purity.

[0034] The prepolymers according to the invention are crosslinkable but are uncrosslinked or at least substantially uncrosslinked; they are furthermore stable, that is to say spontaneous crosslinking by homopolymerisation does not occur.

[0035] The crosslinkable prepolymers of formula (1a) obtainable in accordance with the invention are advantageously liquid or readily meltable or water-soluble; preference is given especially to those prepolymers which are water-soluble. The average molecular weight of the prepolymers according to the invention may vary within wide limits. An average molecular weight of, for example, from 1000 to 50 000 has proved advantageous for the prepolymers according to the invention.

[0036] The prepolymers according to the invention may furthermore be purified in a manner known *per se*, for example by precipitation with acetone, dialysis or ultrafiltration, ultrafiltration being especially preferred. By means of such a purification process the prepolymers according to the invention can be obtained in extremely pure form, for example in the form of solvent-free liquids or melts or in the form of concentrated aqueous solutions that are free or at least substantially free of reaction products, such as salts, and of starting materials or other non-polymeric constituents.

[0037] The preferred method of purifying the prepolymers according to the invention, ultrafiltration, may be carried out in a manner known *per se*. It is possible for the ultrafiltration to be carried out repeatedly, for example from two to ten times. The ultrafiltration may alternatively be carried out continuously until the desired degree of purity has been achieved. The desired degree of purity may, in principle, be as high as desired, and is preferably so selected that the

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content of undesired constituents in the prepolymer is, for example, $\leq 0.001\%$, especially $\leq 0.0001\%$ (1 ppm). The prepolymers may in addition, for example as a result of their synthesis, comprise constituents that are acceptable from the physiological point of view, for example sodium chloride, such constituents advantageously being present in an amount of $\leq 1\%$, especially $\leq 0.1\%$, or more especially $\leq 0.01\%$.

[0038] As has already been mentioned, the prepolymers according to the invention can be crosslinked extremely effectively and in a selective manner, especially by photocrosslinking. The crosslinking may be carried out in the presence or, preferably, in the absence of an additional vinyl comonomer. The crosslinked polymers are water-insoluble.

[0039] Suitably, a photoinitiator that is able to initiate free-radical crosslinking is added in the photocrosslinking process. Examples of photoinitiators are familiar to the person skilled in the art, but suitable photoinitiators that may be mentioned specifically are benzoin methyl ether, 1-hydroxycyclohexylphenylketone, Darocure 1173 and Irgacure types. The crosslinking may then be triggered by actinic radiation, such as, for example, W light, or ionising radiation, such as, for example, gamma radiation or X-ray radiation.

[0040] The photopolymerisation may be carried out without the addition of a solvent, for example when the prepolymer is liquid or readily meltable, or is carried out in a suitable solvent. A suitable solvent is in principle any solvent that dissolves the polymers according to the invention and the vinyl comonomer that may be used in addition, for example water, an alcohol, such as a lower alkanol, for example ethanol or methanol, a carboxylic acid amide, such as dimethylformamide, or dimethyl sulfoxide, or also a mixture of suitable solvents, for example a mixture of water with an alcohol, for example a water/ethanol or water/methanol mixture.

[0041] The photocrosslinking is preferably carried out under solventless or substantially solventless conditions or directly from an aqueous solution of the prepolymer according to the invention which can be obtained as a result of the preferred purification step, ultrafiltration, optionally after the addition of an additional vinyl comonomer. For example the photocrosslinking of an approximately 15 to 90 % aqueous solution may be carried out.

[0042] The process for the preparation of the crosslinked polymers according to the invention comprises, for example, photocrosslinking a prepolymer of formula (1a) according to the invention, especially in substantially pure form, that is to say, for example, after single or repeated ultrafiltration, under solventless or substantially solventless conditions, or in solution, especially in aqueous solution, in the presence or, preferably, in the absence of an additional vinyl comonomer, preferably using a photoinitiator.

[0043] The vinyl comonomer that may, in accordance with the invention, be used in addition in the photocrosslinking may be hydrophilic or hydrophobic or may be a mixture of a hydrophobic and a hydrophilic vinyl monomer. Suitable vinyl monomers include especially those customarily used in the manufacture of contact lenses. A hydrophilic vinyl monomer is to be understood as meaning a monomer that typically yields as homopolymer a polymer that is water-soluble or is capable of absorbing at least 10 % by weight of water. Analogously, a hydrophobic vinyl monomer is to be understood as meaning a monomer that typically yields as homopolymer a polymer that is water-insoluble and is capable of absorbing less than 10 % by weight of water.

[0044] Preference is given to the use of a hydrophobic vinyl comonomer, or a mixture of a hydrophobic vinyl comonomer with a hydrophilic vinyl comonomer, the mixture comprising at least 50 % by weight of a hydrophobic vinyl comonomer. It is possible in that manner for the mechanical properties of the polymer to be improved without the water content being appreciably reduced. In principle, however, both conventional hydrophobic vinyl comonomers and conventional hydrophilic vinyl comonomers are suitable for the copolymerisation with the prepolymers according to the invention.

[0045] Suitable hydrophobic vinyl comonomers include, without this list being exhaustive, C₁-C₁₈-alkyl acrylates and methacrylates, C₃-C₁₈alkyl acrylamides and methacrylamides, acrylonitrile, methacrylonitrile, vinyl-C₁-C₁₈alkanoates, C₂-C₁₈alkenes, C₂-C₁₈haloalkenes, styrene, C₁-C₆alkylstyrene, vinyl alkyl ethers in which the alkyl moiety has from 1 to 6 carbon atoms, C₂-C₁₀perfluoroalkyl acrylates and methacrylates or corresponding partially fluorinated acrylates and methacrylates, C₃-C₁₂perfluoroalkylethylthiocarbonylaminoethyl acrylates and methacrylates, acryloxy- and methacryloxy-alkylsiloxanes, N-vinylcarbazole, and C₁-C₁₂alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like. Preference is given, for example, to C₁-C₄alkyl esters of vinylically unsaturated carboxylic acids having from 3 to 5 carbon atoms and to vinyl esters of carboxylic acids having up to 5 carbon atoms.

[0046] Examples of suitable hydrophobic vinyl comonomers include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyltoluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl methacrylate, tris-trimethylsilyloxy-silylpropyl methacrylate, 3-methacryloxypropylpentamethyl disiloxane and bis(methacryloxypropyl)tetramethyl disiloxane.

[0047] Suitable hydrophilic vinyl comonomers include, without this list being exhaustive, hydroxy-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, lower alkyl acrylamides and methacrylamides, ethoxylated acrylates and methacrylates, hydroxy-substituted lower alkyl acrylamides and methacrylamides, hydroxy-substituted lower alkyl vinyl ethers, sodium ethylenesulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpro-

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panesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- or 4-vinylpyridine, acrylic acid, methacrylic acid, amino- (the term "amino" also including quaternary ammonium), mono-lower alkylamino- or di-lower alkylamino-lower alkyl acrylates and methacrylates, allyl alcohol and the like. Preference is given, for example, to hydroxy-substituted C₂-C₄alkyl (meth)acrylates, five- to seven-membered N-vinyl lactams, N,N-di-C₁-C₄alkyl (meth)acrylamides and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms.

[0048] Examples of suitable hydrophilic vinyl comonomers include hydroxyethyl methacrylate, hydroxyethyl acrylate, acrylamide, methacrylamide, dimethyl acrylamide, allyl alcohol, vinylpyridine, vinylpyrrolidone, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)acrylamide, and the like.

[0049] Preferred hydrophobic vinyl comonomers are methyl methacrylate and vinyl acetate.

[0050] Preferred hydrophilic vinyl comonomers are 2-hydroxyethyl methacrylate, N-vinylpyrrolidone and acrylamide.

[0051] The processing of the prepolymers in accordance with the invention to form ophthalmic mouldings, especially contact lenses, may be carried out in a manner known *per se*, for example by carrying out the photocrosslinking of the prepolymers according to the invention in a suitable contact lens mould. Further examples of mouldings according to the invention in addition to contact lenses are, for example, intraocular lenses and eye dressings, biomedical mouldings for use in surgery, such as heart valves, artificial arteries or the like, and also films or membranes, for example membranes for controlling diffusion, photostructurable foils for information storage, or photoresist materials, for example membranes or mouldings for etching resist or screen printing resist.

[0052] A preferred process for the production of mouldings comprises the following steps:

- 20 a) introducing into a mould a prepolymer that is liquid at room temperature or melted, corresponds essentially to formula (1a) and is substantially free of solvents, in the presence or, preferably, in the absence of an additional vinyl comonomer and with the addition of a photoinitiator,
- b) initiating the photocrosslinking,
- c) opening the mould, so that the moulding can be removed from the mould.

[0053] A further preferred process for the production of mouldings comprises the following steps:

- 30 a) preparing a substantially aqueous solution of a water-soluble prepolymer that corresponds essentially to formula (1a), in the presence or, preferably, in the absence of an additional vinyl comonomer and with the addition of a photoinitiator,
- b) introducing the resulting solution into a mould,
- c) initiating the photocrosslinking,
- d) opening the mould, so that the moulding can be removed from the mould.

[0054] Processes that are known *per se*, such as especially conventional introduction by metering, especially by dropwise introduction, may be used to introduce the prepolymers according to the invention into a mould. Suitable vinyl comonomers, if present, are the aforementioned comonomers in the described amounts. The vinyl comonomers that may be present are advantageously first of all mixed with the prepolymer according to the invention and then introduced into the mould.

[0055] Appropriate moulds are produced, for example, from polypropylene. Suitable materials for reusable moulds are, for example, quartz, sapphire glass and metals.

[0056] If the mouldings to be produced are contact lenses, the mouldings can be produced in a manner known *per se*, for example in a conventional "spin-casting-mold", as described, for example, in US-A-3 408 429, or in accordance with the so-called full-mold method in a static mould, as described, for example, in US-A-4 347 198.

[0057] The photocrosslinking can be initiated in the mould, for example by actinic radiation, for example by UV light, or ionising radiation, for example gamma radiation or X-rays.

[0058] As has already been mentioned, the photocrosslinking is advantageously carried out in the presence of a photoinitiator that is capable of initiating free-radical crosslinking. The photoinitiator is added to the prepolymers according to the invention advantageously before introduction into the mould, preferably by mixing the polymers and the photoinitiator with one another. The amount of photoinitiator may be selected within wide limits, an amount of up to 0.05 g/g of polymer or especially of up to 0.003 g/g of polymer having proved favourable.

[0059] It should be emphasised that, according to the invention, the crosslinking can be effected in a very short time, for example in ≤ 60 minutes, advantageously in ≤ 20 minutes, especially in ≤ 10 minutes, more especially in ≤ 5 minutes, more especially in from 1 to 60 seconds or most especially in from 1 to 30 seconds.

[0060] The opening of the mould, so that the moulding can be removed from the mould, can be carried out in a manner known *per se*.

[0061] If the moulding produced in accordance with the invention is a contact lens, and if that lens has been produced under solventless conditions from a prepolymer according to the invention that has been purified beforehand, then it

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is usually unnecessary for the removal of the moulding to be followed by purification steps, such as, for example, extraction, because the prepolymers used do not contain any undesired low-molecular-weight constituents; consequently the crosslinked product is also free or substantially free of such constituents and subsequent extraction is unnecessary.

5 The contact lens can accordingly be converted directly into a ready-to-use contact lens in customary manner by hydration. Suitable forms of hydration, by which ready-to-use contact lenses having a wide variety of water contents can be obtained, are known to the person skilled in the art. The contact lens is swelled, for example, in water, in an aqueous salt solution, especially in an aqueous salt solution having an osmolarity of approximately from 200 to 450 milliosmol per 1000 ml (unit: mosm/l), preferably of approximately from 250 to 350 mosm/l or especially of approximately 300 mosm/l, or in a mixture of water or of an aqueous salt solution with a physiologically tolerable polar organic solvent, such as glycerol. The prepolymer is preferably swelled in water or in an aqueous salt solution.

10 [0062] The aqueous salt solutions used for the hydration are advantageously solutions of physiologically tolerable salts, such as the buffer salts customary in the field of contact lens care, for example phosphate salts, or the isotonicising agents customary in the field of contact lens care, such as especially alkali metal halides, for example sodium chloride, or solutions of mixtures thereof. An example of an especially suitable salt solution is a synthetic, preferably buffered, lachrymal fluid that has been matched to natural lachrymal fluid in respect of pH value and osmolarity, for example an unbuffered or preferably buffered, for example phosphate buffer-buffered, sodium chloride solution the osmolarity and pH value of which correspond to the osmolarity and pH value of human lachrymal fluid.

15 [0063] The above-defined hydration liquids are preferably pure, that is to say free or substantially free of undesirable constituents. They are especially pure water or a synthetic lachrymal fluid as described above.

20 [0064] If the moulding produced in accordance with the invention is a contact lens, and if that lens has been produced from an aqueous solution of a prepolymer according to the invention that has been purified beforehand, then the crosslinked product also will not contain any troublesome impurities. Subsequent extraction is accordingly unnecessary. Since the crosslinking is carried out in a substantially aqueous solution, subsequent hydration is also unnecessary. According to an advantageous embodiment, the contact lenses obtainable by that process are hence distinguished by 25 the fact that they are suitable for their intended use without extraction. "Intended use" in this context is to be understood as meaning especially that the contact lenses can be inserted into the human eye.

25 [0065] The contact lenses obtainable according to the invention have a wide range of unusual and extremely advantageous properties, amongst which mention should be made, for example, of their excellent tolerability by the human cornea, which is based on a balance of water content, oxygen permeability and mechanical properties. The contact lenses according to the invention also exhibit a high degree of dimensional stability. No changes in shape can be detected even after autoclaving at, for example, approximately 120°C.

30 [0066] Attention may also be drawn to the fact that the contact lenses according to the invention, that is to say especially those comprising a crosslinked polymer from a prepolymer of formula (1a), can be produced in a very simple and efficient manner compared with the state of the art. This is as a result of several factors. First, the starting materials can be obtained or produced at low cost. Secondly, there is the advantage that the prepolymers are surprisingly stable, so that they can be subjected to a high degree of purification. It is therefore possible to use for the crosslinking a polymer that requires virtually no subsequent purification, such as especially the complicated extraction of unpolymerised constituents. In addition, the crosslinking may be carried out under solventless conditions or in aqueous solution, so that a subsequent exchange of solvent or hydration step is not necessary. Finally, the photopolymerisation is carried 35 out within a short period of time, so that the process of producing the contact lenses according to the invention can be organised to be extraordinarily economical from that point of view also.

40 [0067] All of the above advantages naturally apply not only to contact lenses but also to other mouldings according to the invention. The total effect of the various advantageous aspects in the production of the mouldings according to the invention is that the mouldings according to the invention are suitable especially as mass-produced articles, such 45 as, for example, contact lenses that are worn for a short length of time and are then replaced by new lenses.

[0068] In the following Examples amounts are amounts by weight, unless specified otherwise, and temperatures are given in degrees Celsius. The Examples are not intended to limit the invention in any way, for example to the scope of the Examples.

50 Preparation Examples

[0069] **Example 1:** 4.44 g of isophorone diisocyanate are mixed with 0.026 g of dibutyltin dilaurate and the mixture is heated to 70°C. 17.58 g of polyethylene glycol 1500-diglycidyl diacrylate (reaction product of 1 molar equivalent of polyethylene glycol 1500-diglycidyl ether and 2 molar equivalents of acrylic acid) dissolved in 200 ml of toluene are added dropwise, and the mixture is stirred until the isocyanate content has been reduced to half (approximately 2.5 hours). 9.72 g of polyethylene glycol 400-monomethacrylate, dissolved in 100 ml of dioxane, are then added dropwise and stirring is continued at 70°C until virtually no isocyanate can be detected (isocyanate content ≤ 0.01 equivalent/kg, approximately 12 hours). Finally, the solution is concentrated and the product is precipitated from diethyl ether.

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[0070] **Example 2:** In accordance with the method indicated in Example 1, 4.44 g of isophorone diisocyanate are reacted with 17.58 g of polyethylene glycol 1500-diglycidyl diacrylate and 21.72 g of polyethylene glycol 1000-mono-methacrylate.

5 [0071] **Example 3:** In accordance with the method indicated in Example 1, 8.89 g of isophorone diisocyanate are reacted with 45.12 g of polyethylene glycol 2000-diglycidyl diacrylate and 43.4 g of polyethylene glycol 1000-mono-methacrylate.

10 [0072] **Example 4:** In accordance with the method indicated in Example 1, 7.11 g of isophorone diisocyanate are reacted with 18.3 g of polyethylene glycol 1000-diglycidyl diacrylate and 34.75g of polyethylene glycol 1000-mono-methacrylate.

Application Examples

15 [0073] **Example 5:** 1.2 g of the prepolymer obtained according to Example 1 and 4 mg of Irgacure® 2959 are mixed with 0.8 g of water until a homogeneous clear solution is obtained. A 0.1 mm thick film is produced from the clear viscous solution between two glass plates provided with spacers. The film is irradiated for 10 seconds using a UV lamp. A clear flexible film is obtained which swells in water to form a clear hydrogel having a solids content of 40 %. The elasticity modulus of the swelled film is 4.1 Mpa (measured using a tension measuring apparatus from the company Vitrodyne), and the elongation at tear has a value of from 50 to 100 %.

20 [0074] **Example 6:** 1.2 g of the prepolymer obtained according to Example 2 and 4 mg of Irgacur® 2959 are mixed with 0.8 g of water until a homogeneous clear solution is obtained. A 0.1 mm thick film is produced from the clear viscous solution between two glass plates provided with spacers. The film is exposed for 10 seconds using a UV lamp. A clear flexible film is obtained which swells in water to form a clear hydrogel having a solids content of 32 %. The elasticity modulus of the swollen film is 2.6 Mpa (measured using a tension measuring apparatus from the company Vitrodyne), and the elongation at tear has a value of approximately 45 %.

25 [0075] **Example 7:** 1.2 g of the prepolymer obtained according to Example 3 and 4 mg of Irgacure® 2959 are mixed with 0.8 g of water until a homogeneous clear solution is obtained. A 0.1 mm thick film is produced from the clear viscous solution between two glass plates provided with spacers. The film is exposed for 10 seconds using a UV lamp. A clear flexible film is obtained which swells in water to form a clear hydrogel having a solids content of 26 %. The elasticity modulus of the swollen film is 1.2 Mpa (measured using a tension measuring apparatus from the company Vitrodyne), and the elongation at tear has a value of approximately 40 %.

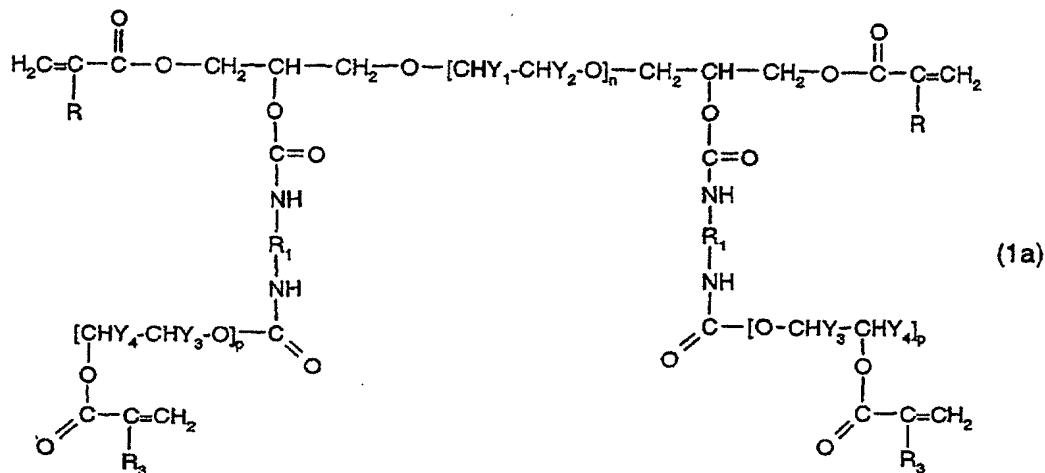
30 [0076] **Example 8:** 1 g of the prepolymer obtained according to Example 4 and 4 mg of Irgacure® 2959 are mixed with 1 g of water until a homogeneous clear solution is obtained. A 0.1 mm thick film is produced from the clear viscous solution between two glass plates provided with spacers. The film is exposed for 10 seconds using a UV lamp. A clear flexible film is obtained which swells in water to form a clear hydrogel having a solids content of 25 %. The elasticity modulus of the swollen film is 1.4 Mpa (measured using a tension measuring apparatus from the company Vitrodyne), and the elongation at tear has a value of from 80 to 120%.

35 [0077] **Example 9:** 4 mg of Irgacure® 2959 are dissolved in 1g of the prepolymer obtained according to Example 4. A 0.1 mm thick film is produced from the clear viscous solution between two glass plates provided with spacers. The film is exposed for 10 seconds using a UV lamp. A clear flexible film is obtained which swells in water to form a clear hydrogel having a solids content of 47 %.

Claims

45 1. A contact lens, obtainable by crosslinking in a mould a prepolymer that corresponds essentially to formula

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wherein

R and R₃ are each independently of the other hydrogen or methyl,
 one of the radicals Y₁ and Y₂ is hydrogen and the other is hydrogen or methyl,
 25 R₁ is the radical of a linear or branched aliphatic diisocyanate having from 3 to 24 carbon atoms, the radical of a cycloaliphatic or aliphatic-cycloaliphatic diisocyanate having from 3 to 24 carbon atoms, or the radical of an aromatic or araliphatic diisocyanate having from 6 to 24 carbon atoms,
 one of the radicals Y₃ and Y₄ is hydrogen and the other is hydrogen or methyl,
 30 p is an integer from 5 to 100 and
 n is an integer from 5 to 100,

in the absence or presence of an additional vinyl comonomer.

2. A contact lens according to claim 1, wherein Y₁ and Y₂ in formula (1a) are each hydrogen.
3. A contact lens according to claim 1 or 2, wherein R₁ is linear or branched C₃-C₁₈alkylene or unsubstituted or C₁-C₄alkyl- or C₁-C₄alkoxy-substituted C₆-C₁₀arylene, C₇-C₁₈aralkylene, C₆-C₁₀arylene-C₁-C₂alkylene-C₆-C₁₀arylene, C₃-C₈cycloalkylene, C₃-C₈cycloalkylene-C₁-C₆alkylene, C₃-C₈cycloalkylene-C₁-C₂alkylene-C₃-C₈cycloalkylene or C₁-C₆alkylene-C₃-C₈cycloalkylene-C₁-C₆alkylene.
4. A contact lens according to any one of claims 1 to 3, wherein R₁ is linear or branched C₆-C₁₀alkylene, cyclohexylenemethylene or cyclohexylenemethylenecyclohexylene unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, or phenylene or phenylenemethylenephenylenne unsubstituted or substituted in the phenyl moiety by methyl.
5. A contact lens according to any one of claims 1 to 4, wherein R₁ is asymmetrical, branched C₆-C₁₀alkylene, or cyclohexylenemethylene substituted in the cyclohexyl moiety by from 1 to 3 methyl groups.
6. A contact lens according to any one of claims 1 to 5 wherein Y₃ and Y₄ are each hydrogen.
7. A contact lens according to claim 1, wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is linear or branched C₆-C₁₀alkylene, cyclohexylenemethylene or cyclohexylenemethylenecyclohexylene unsubstituted or substituted in the cyclohexyl moiety from from 1 to 3 methyl groups, or phenylene or phenylenemethylenephenylenne unsubstituted or substituted in the phenyl moiety by methyl, Y₁, Y₂, Y₃ and Y₄ are each hydrogen, and n and p are each independently of the other an integer from 8 to 50.
8. A contact lens according to claim 1, wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is asymmetrical, branched C₆-C₁₀alkylene, or cyclohexylenemethylene substituted in the cyclohexyl moiety by

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from 1 to 3 methyl groups, Y₁, Y₂, Y₃ and Y₄ are each hydrogen, and n and p are each independently of the other an integer from 9 to 25.

5 9. A contact lens according to any one of claims 1 to 8, wherein the crosslinking of the prepolymer takes place in the absence of an additional vinyl comonomer.

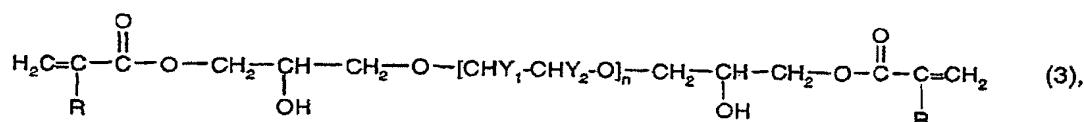
10 10. A contact lens according to any one of claims 1 to 9, wherein the prepolymer in substantially pure form is photo-crosslinked in aqueous solution in the absence of an additional vinyl comonomer using a photoinitiator.

15 11. A prepolymer, which corresponds essentially to formula (1 a) given in claim 1.

12. A prepolymer according to claim 11, wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is linear or branched C₆-C₁₀alkylene, cyclohexylenemethylene or cyclohexylenemethylenecyclohexylene unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, or phenylene or phenylenemethylenephenylene unsubstituted or substituted in the phenyl moiety by methyl, Y₁, Y₂, Y₃ and Y₄ are each hydrogen and n and p are each independently of the other an integer from 8 to 50.

20 13. A prepolymer according to claim 11, wherein R and R₃ are each independently of the other hydrogen or methyl, R₁ is asymmetrical, branched C₆-C₁₀alkylene, or cyclohexylenemethylene substituted in the cyclohexyl moiety by from 1 to 3 methyl groups, Y₁, Y₂, Y₃ and Y₄ are each hydrogen and n and p are each independently of the other an integer from 9 to 25.

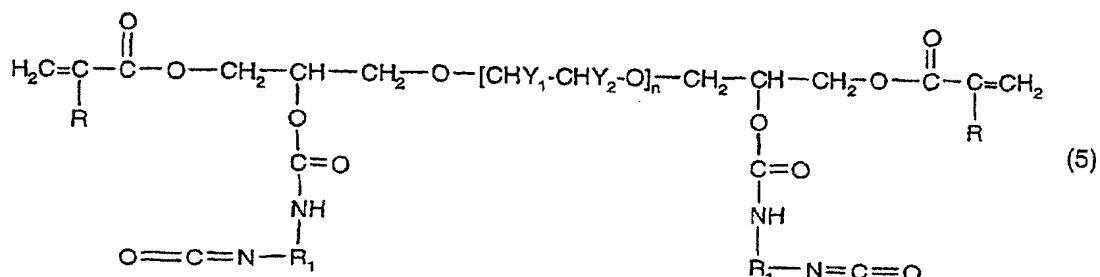
25 14. A process for the preparation of a prepolymer of formula (1a) according to claim 1, wherein approximately 1 molar equivalent of a compound of formula



35 wherein R, Y₁, Y₂ and n are each as defined in claim 1, is reacted with approximately 2 molar equivalents of a diisocyanate of formula



40 wherein R₁ is as defined in claim 1, and the addition product of formula

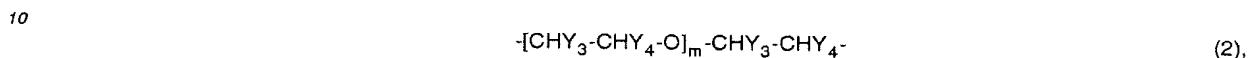


55 obtainable in that process is then reacted with approximately 2 molar equivalents of a compound of formula

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wherein R_2 is a radical of formula



one of the radicals Y_3 and Y_4 is hydrogen and the other is hydrogen or methyl, m is an integer from 4 to 99, and
15 R_3 is as defined in claim 1,
to form a prepolymer of formula (1a) according to the invention.

15. A polymer, obtainable by crosslinking a prepolymer according to any one of claims 11 to 13 in the absence or presence of an additional vinyl comonomer.

20 16. A process for the production of a moulding, which comprises the following steps:

25 a) introducing into a mould a prepolymer of formula (1a) according to claim 1 that is liquid at room temperature or melted and is substantially free of solvents, in the absence or presence of an additional vinyl comonomer and with the addition of a photoinitiator,
b) initiating the photocrosslinking,
c) opening the mould, so that the moulding can be removed from the mould.

17. A process according to claim 16, wherein the process is carried out in the absence of an additional vinyl comonomer.

30 18. A process for the production of mouldings, which comprises the following steps:

35 a) preparing a substantially aqueous solution of a water-soluble prepolymer of formula (1a) according to claim 1 in the absence or presence of an additional vinyl comonomer and with the addition of a photoinitiator,
b) introducing the resulting solution into a mould,
c) initiating the photocrosslinking,
d) opening the mould, so that the moulding can be removed from the mould.

19. A process according to claim 18 carried out in the absence of an additional vinyl comonomer.

40 20. A process according to any one of claims 16 to 19, wherein the moulding is a contact lens.

21. A moulding, especially a contact lens, obtainable in accordance with the process according to any one of claims 16 to 19.

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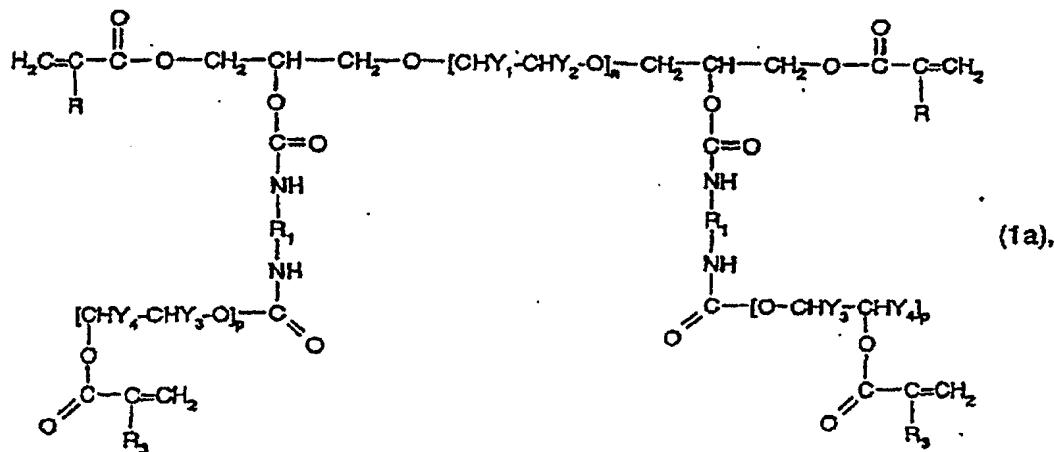
Patentansprüche

1. Kontaktlinse, erhältlich durch Vernetzen eines Präpolymeren, das im wesentlichen der nachstehenden Formel entspricht, in einer Form

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20 wobei

R und R₃ jeweils unabhängig voneinander Wasserstoff oder Methyl bedeuten,
einer der Reste Y₁ und Y₂ Wasserstoff und der andere Wasserstoff oder Methyl bedeuten,
R₁ den Rest eines linearen oder verzweigten aliphatischen Diisocyanats mit 3 bis 24 Kohlenstoffatomen, den
Rest eines cycloaliphatischen oder aliphatisch-cycloaliphatischen Diisocyanats mit 3 bis 24 Kohlenstoffatomen
oder den Rest eines aromatischen oder araliphatischen Diisocyanats mit 6 bis 24 Kohlenstoffatomen
bedeutet,
einer der Reste Y₃ und Y₄ Wasserstoff und der andere Wasserstoff oder Methyl bedeuten,
p eine ganze Zahl mit einem Wert von 5 bis 100 bedeutet und
n eine ganze Zahl mit einem Wert von 5 bis 100 bedeutet,

in Abwesenheit oder Gegenwart eines zusätzlichen Vinyl-Comonomeren.

2. Kontaktlinse nach Anspruch 1, wobei Y₁ und Y₂ in der Formel (1a) jeweils Wasserstoff bedeuten.
3. Kontaktlinse nach Anspruch 1 oder 2, wobei R₁ lineares oder verzweigtes C₃-C₁₈-Alkylen oder unsubstituiertes oder mit C₁-C₄-Alkyl oder C₁-C₄-Alkoxy substituiertes C₆-C₁₀-Arylen, C₇-C₁₈-Aralkylen, C₆-C₁₀-Arylen-C₁-C₂-alkylen-C₆-C₁₀-arylen, C₃-C₈-Cycloalkylen, C₃-C₈-Cycloalkylen-C₁-C₆-alkylen, C₃-C₈-Cycloalkylen-C₁-C₂-alkylen-C₃-C₈-cycloalkylen oder C₁-C₆-Alkylen-C₃-C₈-cycloalkylen-C₁-C₆-alkylen bedeutet.
4. Kontaktlinse nach einem der Ansprüche 1 bis 3, wobei R₁ lineares oder verzweigtes C₆-C₁₀-Alkylen, Cyclohexylenmethylene oder Cyclohexylenmethylencyclohexylen, die unsubstituiert oder im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert sind, oder Phenylen oder Phenylmethylenphenylen, die unsubstituiert oder im Phenylrest mit Methyl substituiert sind, bedeutet.
5. Kontaktlinse nach einem der Ansprüche 1 bis 4, wobei R₁ asymmetrisches, verzweigtes C₆-C₁₀-Alkylen oder Cyclohexylenmethylene, das im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert ist, bedeutet.
6. Kontaktlinse nach einem der Ansprüche 1 bis 5, wobei Y₃ und Y₄ jeweils Wasserstoff bedeuten.
7. Kontaktlinse nach Anspruch 1, wobei R und R₃ jeweils unabhängig voneinander Wasserstoff oder Methyl bedeuten, R₁ lineares oder verzweigtes C₆-C₁₀-Alkylen, Cyclohexylenmethylene oder Cyclohexylenmethylencyclohexylen, die unsubstituiert oder im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert sind, oder Phenylen oder Phenylmethylenphenylen, die unsubstituiert oder im Phenylrest mit Methyl substituiert sind, bedeuten, Y₁, Y₂, Y₃ und Y₄ jeweils Wasserstoff bedeuten und n und p jeweils unabhängig voneinander ganze Zahlen mit einem Wert von 8 bis 50 bedeuten.
8. Kontaktlinse nach Anspruch 1, wobei R und R₃ jeweils unabhängig voneinander Wasserstoff oder Methyl bedeuten,

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R_1 asymmetrisches, verzweigtes C₆-C₁₀-Alkylen oder Cyclohexylenmethylen, das im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert ist, bedeutet, Y₁, Y₂, Y₃ und Y₄ jeweils Wasserstoff bedeuten und n und p jeweils unabhängig voneinander ganze Zahlen mit einem Wert von 9 bis 25 bedeuten.

5 9. Kontaktlinse nach einem der Ansprüche 1 bis 8, wobei die Vernetzung des Präpolymeren in Abwesenheit eines zusätzlichen Vinylcomonomeren stattfindet.

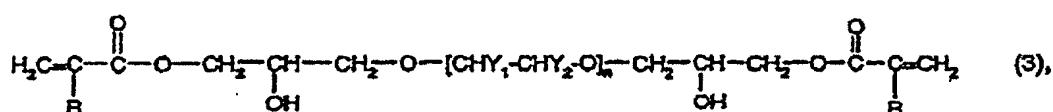
10 10. Kontaktlinse nach einem der Ansprüche 1 bis 9, wobei das Präpolymere in im wesentlichen reiner Form in wässriger Lösung in Abwesenheit eines zusätzlichen Vinylcomonomeren unter Verwendung eines Photoinitiators vernetzt worden ist.

15 11. Präpolymeres, das im wesentlichen der in Anspruch 1 angegebenen Formel (1a) entspricht.

12. Präpolymeres nach Anspruch 11, wobei R und R₃ jeweils unabhängig voneinander Wasserstoff oder Methyl bedeuten, R₁ lineares oder verzweigtes C₆-C₁₀-Alkylen, Cyclohexylenmethylen oder Cyclohexylenmethyleneencyclohexylen, die unsubstituiert oder im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert sind, oder Phenylen oder Phenylenmethylenephenylene, die unsubstituiert oder im Phenylrest mit Methyl substituiert sind, bedeutet, Y₁, Y₂, Y₃ und Y₄ jeweils Wasserstoff bedeuten und n und p jeweils unabhängig voneinander ganze Zahlen mit einem Wert von 8 bis 50 bedeuten.

20 13. Präpolymeres nach Anspruch 11, wobei R und R₃ jeweils unabhängig voneinander Wasserstoff oder Methyl bedeuten, R₁ asymmetrisches, verzweigtes C₆-C₁₀-Alkylen oder Cyclohexylenmethylen, das im Cyclohexylrest mit 1 bis 3 Methylgruppen substituiert ist, bedeutet, Y₁, Y₂, Y₃ und Y₄ jeweils Wasserstoff bedeuten und n und p jeweils unabhängig voneinander ganze Zahlen mit einem Wert von 9 bis 25 bedeuten.

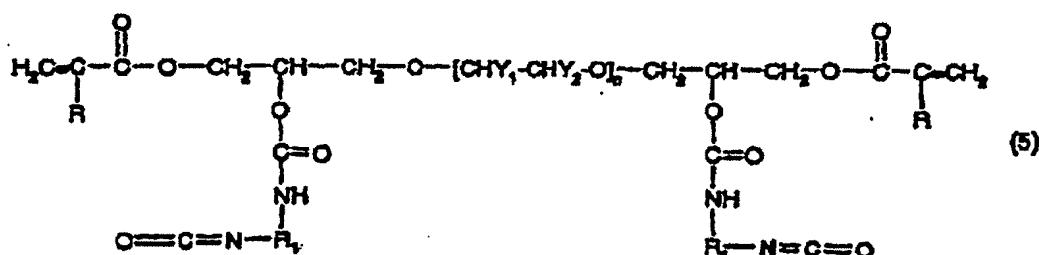
25 14. Verfahren zur Herstellung eines Präpolymeren der Formel (1a) gemäß Anspruch 1, wobei etwa 1 Moläquivalent einer Verbindung der Formel



worin R, Y₁, Y₂ und n jeweils die in Anspruch 1 definierten Bedeutungen haben, mit etwa 2 Moläquivalenten eines Diisocyanats der Formel

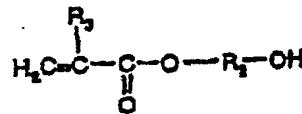


worin R_1 die in Anspruch 1 definierte Bedeutung hat, umgesetzt wird und das Additionsprodukt der Formel



das in diesem Verfahren erhältlich ist, anschließend mit etwa 2 Moläquivalenten einer Verbindung der Formel

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worin R_2 einen Rest der Formel

10 $-\text{[CHY}_3\text{-CHY}_4\text{-O}]_m\text{-CHY}_3\text{-CHY}_4-$ (2)

15 bedeutet, einer der Reste Y_3 und Y_4 Wasserstoff und der andere Wasserstoff oder Methyl bedeutet, m eine ganze Zahl mit einem Wert von 4 bis 99 bedeutet und R_3 die in Anspruch 1 definierte Bedeutung hat, unter Bildung eines erfindungsgemäßen Präpolymeren der Formel (1a) umgesetzt wird.

16. Polymeres, erhältlich durch Vernetzung eines Präpolymeren nach einem der Ansprüche 11 bis 13 in Abwesenheit oder Gegenwart eines zusätzlichen Vinylcomonomeren.

20 16. Verfahren zur Herstellung eines Formkörpers, umfassend die folgenden Stufen:

a) in eine Form wird gemäss Anspruch 1 ein Präpolymeres der Formel (1a), das bei Raumtemperatur flüssig ist oder geschmolzen ist, und das im wesentlichen frei von Lösungsmitteln ist, in Abwesenheit oder in Gegenwart eines zusätzlichen Vinylcomonomeren und unter Zugabe eines Photoinitiators gegeben,
 25 b) die Photovernetzung wird initiiert und
 c) die Form wird geöffnet, so dass der Formkörper aus der Form entnommen werden kann.

17. Verfahren nach Anspruch 16, wobei das Verfahren in Abwesenheit eines zusätzlichen Vinylcomonomeren durchgeführt wird.

30 18. Verfahren zur Herstellung von Formkörpern, umfassend die folgenden Stufen:

a) es wird eine im wesentlichen wässrige Lösung eines wasserlöslichen Präpolymeren der Formel (1a) nach Anspruch 1, in Abwesenheit oder in Gegenwart eines zusätzlichen Vinylcomonomeren und unter Zugabe eines Photoinitiators hergestellt,
 35 b) die erhaltene Lösung wird in eine Form gegeben,
 c) die Photovernetzung wird initiiert und
 d) die Form wird geöffnet, so dass der Formkörper aus der Form entnommen werden kann.

19. Verfahren nach Anspruch 18, das in Abwesenheit eines zusätzlichen Vinylcomonomeren durchgeführt wird.

40 20. Verfahren nach einem der Ansprüche 16 bis 19, wobei es sich beim Formkörper um eine Kontaktlinse handelt.

21. Formkörper, insbesondere eine Kontaktlinse, erhältlich nach dem Verfahren gemäß einem der Ansprüche 16 bis 19.

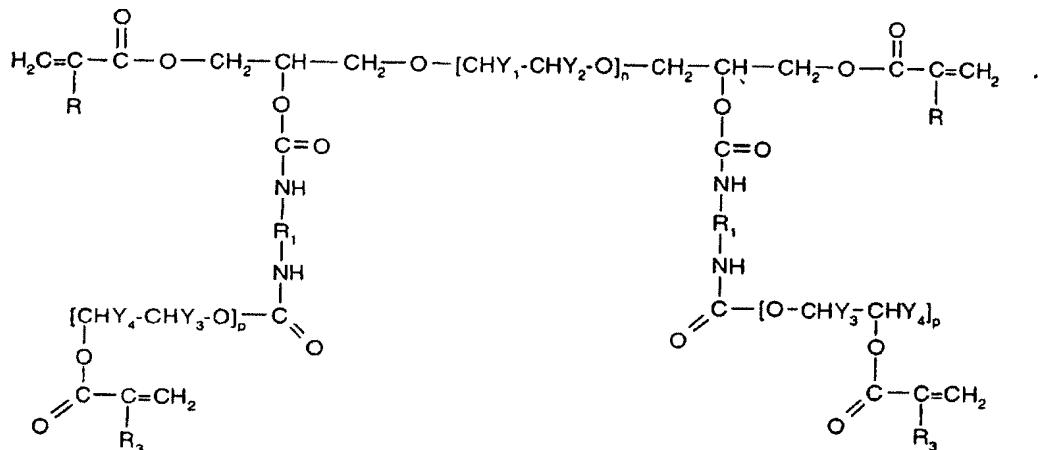
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Revendications

50 1. Une lentille de contact, pouvant être obtenue par réticulation dans un moule d'un pré-polymère qui correspond essentiellement à la formule

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où

R et R_3 signifient chacun indépendamment de l'autre, l'hydrogène ou un groupe méthyle,
 l'un des radicaux Y_1 et Y_2 signifie l'hydrogène et l'autre signifie l'hydrogène ou un groupe méthyle,
 R_1 signifie le radical d'un diisocyanate aliphatique linéaire ou ramifié ayant de 3 à 24 atomes de carbone, le
 radical d'un diisocyanate cycloaliphatique ou aliphatique-cycloaliphatique ayant de 3 à 24 atomes de carbone
 ou le radical d'un diisocyanate aromatique ou araliphatique ayant de 6 à 24 atomes de carbone,
 l'un des radicaux Y_3 et Y_4 signifie l'hydrogène et l'autre signifie l'hydrogène ou un groupe méthyle,
 p signifie un nombre entier de 5 à 100 et
 n signifie un nombre entier de 5 à 100.

en l'absence ou en présence d'un comonomère vinylique supplémentaire.

2. Une lentille de contact selon la revendication 1, où Y_1 et Y_2 dans la formule (1a) signifient chacun l'hydrogène.
3. Une lentille de contact selon la revendication 1 ou 2, où R_1 signifie un groupe C_3-C_{18} alkylène linéaire ou ramifié
 ou un groupe C_6-C_{10} arylène non substitué ou C_1-C_4 alkyl- ou C_1-C_4 alcoxy-substitué, un groupe C_7-C_{18} aralkylène,
 C_6-C_{10} arylène- C_1-C_2 alkylène- C_6-C_{10} arylène, C_3-C_8 cycloalkylène, C_3-C_8 cycloalkylène- C_1-C_6 alkylène, C_3-C_8 cy-
 cloalkylène- C_1-C_2 alkylène- C_3-C_8 cycloalkylène ou C_1-C_6 alkylène- C_3-C_8 cycloalkylène- C_1-C_6 alkylène.
4. Une lentille de contact selon l'une quelconque des revendications 1 à 3, où R_1 signifie un groupe C_6-C_{10} alkylène
 linéaire ou ramifié, cyclohexyléneméthylène ou cyclohexyléneméthylénecyclohexylène non substitué ou substitué
 dans le reste cyclohexyle par 1 à 3 groupes méthyle, ou bien un groupe phénylène ou phényléneméthylénephé-
 nylène non substitué ou substitué dans le reste phényle par un groupe méthyle.
5. Une lentille de contact selon l'une quelconque des revendications 1 à 4, où R_1 signifie un groupe C_6-C_{10} alkylène
 asymétrique, ramifié, ou un groupe cyclohexyléneméthylène substitué dans le reste cyclohexyle par 1 à 3 groupes
 méthyle.
6. Une lentille de contact selon l'une quelconque des revendications 1 à 5, où Y_3 et Y_4 signifient chacun l'hydrogène.
7. Une lentille de contact selon la revendication 1, où R et R_3 signifient chacun indépendamment de l'autre l'hydrogène
 ou un groupe méthyle, R_1 signifie un groupe C_6-C_{10} alkylène linéaire ou ramifié, cyclohexyléneméthylène ou cy-
 clohexyléneméthylénecyclohexylène non substitué ou substitué dans le reste cyclohexyle par 1 à 3 groupes méthyle,
 ou un groupe phénylène ou phényléneméthylénephényle non substitué ou substitué dans le reste phényle
 par un groupe méthyle, Y_1 , Y_2 , Y_3 et Y_4 signifient chacun l'hydrogène, et n et p signifient chacun indépendamment

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de l'autre, un nombre entier de 8 à 50.

5 8. Une lentille de contact selon la revendication 1, où R et R₃ signifient chacun indépendamment de l'autre l'hydrogène ou un groupe méthyle, R₁ signifie un groupe C₆-C₁₀alkylène asymétrique, ramifié ou cyclohexylèneméthylène substitué dans le reste cyclohexyle par 1 à 3 groupes méthyle, Y₁, Y₂, Y₃ et Y₄ signifient chacun l'hydrogène, et n et p signifient chacun indépendamment de l'autre, un nombre entier de 9 à 25.

10 9. Une lentille de contact selon l'une quelconque des revendications 1 à 8, où la réticulation du pré-polymère s'effectue en l'absence d'un comonomère vinylique supplémentaire.

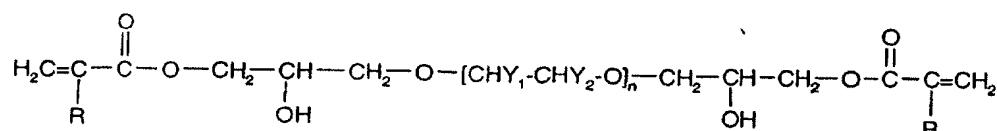
15 10. Une lentille de contact selon l'une quelconque des revendications 1 à 9, où le pré-polymère sous forme实质iellement pure est photoréticulé dans une solution aqueuse en l'absence d'un comonomère vinylique supplémentaire en utilisant un photoinitiateur.

20 11. Un pré-polymère qui correspond essentiellement à la formule (1a) donnée à la revendication 1.

25 12. Un pré-polymère selon la revendication 11, où R et R₃ signifient chacun indépendamment de l'autre l'hydrogène ou un groupe méthyle, R₁ signifie un groupe C₆-C₁₀alkylène linéaire ou ramifié, cyclohexylèneméthylène ou cyclohexylèneméthylène non substitué ou substitué dans le reste cyclohexyle par 1 à 3 groupes méthyle, ou un groupe phénylène ou phénylèneméthylènephénylène non substitué ou substitué dans le reste phényle par un groupe méthyle, Y₁, Y₂, Y₃ et Y₄ signifient chacun l'hydrogène et n et p signifient chacun indépendamment de l'autre, un nombre entier de 8 à 50.

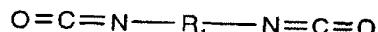
30 13. Un pré-polymère selon la revendication 11, où R et R₃ signifient chacun indépendamment de l'autre l'hydrogène ou un groupe méthyle, R₁ signifie un groupe C₆-C₁₀alkylène asymétrique, ramifié ou cyclohexylèneméthylène substitué dans le reste cyclohexyle par 1 à 3 groupes méthyle, Y₁, Y₂, Y₃ et Y₄ signifient chacun l'hydrogène et n et p signifient chacun indépendamment de l'autre, un nombre entier de 9 à 25.

35 14. Un procédé de préparation d'un pré-polymère de formule (1a) selon la revendication 1, où environ 1 équivalent molaire d'un composé de formule



(3),

40 où R, Y₁, Y₂ et n sont chacun tels que définis à la revendication 1, est mis à réagir avec environ 2 équivalents molaires d'un diisocyanate de formule

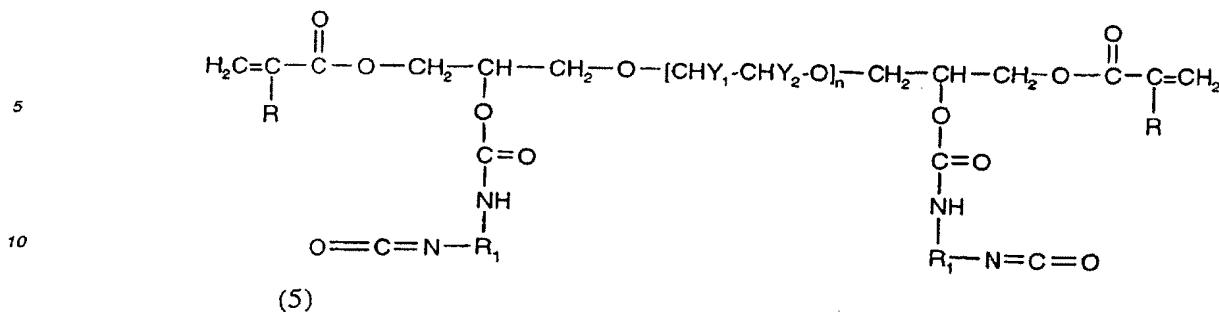


(4)

50 où R₁ est tel que défini à la revendication 1, et le produit d'addition de formule

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15 pouvant être obtenu dans ce procédé est ensuite mis à réagir avec environ 2 équivalents molaires d'un composé de formule



25 (6)

où R_2 signifie un radical de formule



35 l'un des radicaux Y_3 et Y_4 signifie l'hydrogène et l'autre signifie l'hydrogène ou un groupe méthyle, m signifie un nombre entier de 4 à 99, et R_3 est tel que défini à la revendication 1, pour former un pré-polymère de formule (1a) de l'invention.

40 15. Un polymère pouvant être obtenu par réticulation d'un pré-polymère selon l'une quelconque des revendications 11 à 13, en l'absence ou en présence d'un comonomère vinylique supplémentaire.

16. Un procédé de production d'un moulage, qui comprend les étapes suivantes:

45 a) on introduit dans un moule un pré-polymère de formule (1a) selon la revendication 1, qui est liquide à la température ambiante ou fondu et est substantiellement exempt de solvants, en l'absence ou en présence d'un comonomère vinylique supplémentaire et avec addition d'un photoinitiateur,
b) on provoque la photoréticulation,
c) on ouvre le moule, pour pouvoir retirer le moulage du moule.

50 17. Un procédé selon la revendication 16, où le procédé est effectué en l'absence d'un comonomère vinylique supplémentaire.

18. Un procédé de production de moulages, qui comprend les étapes suivantes:

55 a) on prépare une solution substantiellement aqueuse d'un pré-polymère soluble dans l'eau de formule (1a) selon la revendication 1, en l'absence ou en présence d'un comonomère vinylique supplémentaire et avec addition d'un photoinitiateur,
b) on introduit la solution résultante dans un moule,

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- c) on provoque la photoréticulation,
- d) on ouvre le moule, pour pouvoir retirer le moulage du moule.

19. Un procédé selon la revendication 18 effectué en l'absence d'un comonomère vinylique supplémentaire.

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20. Un procédé selon l'une quelconque des revendications 16 à 19, où le moulage est une lentille de contact.

21. Un moulage, spécialement une lentille de contact, pouvant être obtenue avec le procédé selon l'une quelconque
des revendications 16 à 19.

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